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Comparative Study of Polyacrylamide Co-polymers for EOR at High Salinity Conditions "Laboratory and Simulation

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SUMMARY

The success of polymer flooding as a method of oil recovery has been attributed to a profile control mechanism of the displacing fluid (polymer solutions) related to the displaced fluid (crude oil), depending on properties such as polymer viscosity and its dependence with reservoir and flow conditions. The viscosity of polymer flow depends not only on the size of the molecules or molecular weight but it is further affected by salinity and divalent content on the brine used for the preparation of the polymer slug. The effect of salinity on polymer viscosity is more critical in presence of divalent ions Ca2+ and Mg2+ and high salinity conditions, which limits the use high salinity produced water for re-injection in polymer flooding processes where high salinity is involved. A series of salinity resistant polymers have been developed by incorporating co-monomers including hydrophilic and hydrophobic groups or combination of them along the chain of polyacrylamide which has made the viscosity behavior more complex and affected by ionic interactions both intra-molecular and inter-molecular. Therefore, an extensively screening process that includes evaluation of variables such as: stability of polymer solutions under salinity and ion composition, flow conditions and sensitivity analysis using simulation according to specific applications, is required for the selection of any specific system.

A systematic comparative study of the screening of commercial partial hydrolysed polyacrylamide (PHPA), and co-polymers of acrylamide and hydrophobic modified Comb-polymers (HMPAM) under high salinity conditions is investigated. Synthetic high salinity and multi-component (with divalent ions) produced water from a North Sea reservoir was used on Bernheimer sandstone core samples using a crude oil from the North Sea with specific gravity 21 ºAPI. Results from core flooding and rheology were matched to obtain required mathematical correlations to simulate core flooding experiments numerically and compare the efficiency of the different polymers.

While polymers PHPA and co-polymers AM-AMPS and AM-nVP showed typical Newtonian behavior at low shear rates and non- Newtonian at high shear rates, HMPAM polymers have shear thinning behavior. Newtonian behavior on PHPA-3 seems to support its higher recovery factor comparing with PHPA-6 (higher MW). Viscosity of HMPAM solutions is more sensitive to changes of the polymer concentration and more sensible to flow conditions. Additionally, ionic interactions and steric effects in the co-polymers contribute the efficiency of the oil recovery at high salinity. Therefore, their viscosity behavior needs to be evaluated.

Introduction

Polymer flooding is the more successfully and mature chemical EOR technique (Manrique, 2007), it has been mainly applied on sandstone but also in carbonate (limestone and dolomite) reservoirs (Oil and Gas Survey, 2014; Sheng, 2012 and Vermolen, 2011). The amount of oil remaining trapped inside the pore structure is affected by the balance between viscous and capillary forces (Karpan, 2011). The success of polymer flooding as a method of oil recovery has been attributed to a profile control mechanism between polymer solution and oil during water flooding. Two important parameters are important on this process: Mobility Ratio (M) and Capillary Number (Nc) (Thomas, 2007). Mobility ratio is defined as the ratio of mobility between displacing fluid (water or chemical slug) and displaced fluid (oil), while Capillary Number is the ratio between viscous and capillary forces, and is inversely proportional to the interfacial tension according to the following expression:

$$N_c = \frac{v\mu}{\sigma} \quad \frac{Viscosity\ Forces}{Capillary\ Forces} \tag{1}$$

$$M = \frac{\lambda_{displacing\ fluid}}{\lambda_{displaced\ fluid}} \qquad \lambda = \frac{k}{\mu} \tag{2}$$

Where:

K: Effective Permeability (m^2) σ: Interfacial Tension (N/m)

V: Darcy Velocity (m/sec) μ: Viscosity of fluid concerned (Pa.s)

Increasing the capillary number has resulted in an increase in oil recovery (Thomas, 2008). As polymers increase viscosity forces they will affect the capillary number, however the major effect of the polymer is on the mobility ratio. Polymers modify the viscosity of the displacing fluid and minimize the presence of viscous fingering in the porous medium during water flooding thus decreasing the mobility ratio.

It is possible to increase the sweeping efficiency of the polymer flooding by tailoring polymer viscosity according to the viscosity of the crude oil to have a mobility ratio lower than one, which has been described by Thomas (2008) as favorable mobility ratio. However, as polymers are injected in the reservoir, they are exposed to chemical, physical and mechanical degradation which negatively affect their performance in sweeping the crude oil trapped in the porous medium. These effects have been reported to be critical under high salinity brine with divalent ions Ca^{2+} and Mg^{2+} and temperature conditions (Levitt, 2009). Polymers type HPAM (partially hydrolysed poly-acrylamide) are the most common polymers applied in chemical EOR because of its cost and wider range of available molecular weight for different applications (Sheng, 2011). However, the viscosity of this polymer is highly affected by brine salinity and hardness (content of divalent ions Ca^{2+} and Mg^{2+}).

In recent years, more polymers have been developed to provide solutions for temperature and higher salinity applications, between them are: copolymers, ter-polymers and hydrophobic modified polymers comb-shaped polymer from polyacrylamide.

The structure of polymers has been tailored to enhance ionic interaction in aqueous solutions, for example: resistance to salinity and to interactions with divalent ions (hardness) has been improved by incorporating hydrophobic monomers C8-C12-alkyl and monomers with a different functional group along the polyacrylamide chain in the composition of HPAM. Moreover, in some cases, other monomers such as 2-acrylamido-2-Methyl propane Sulfonate (AMPS) have been incorporated to the polymer to include functional groups along the polyacrylamide chain (Lewit, 2008). Examples of these co-polymers are type AM-AMPS and AM-nVP respectively. Furthermore, there are also the type comb polymers which are hydrophobic modified polyacrylamide (HMPAM) made by incorporating both hydrophobic and hydrophilic groups into the short side branches along with the main chain of the co-polymer as is shown in figure 1, A contains a hydrophilic group and R1, R2, R3

and R4 are hydrophobic groups (Sheng, 2011). These polymers have reported higher viscosity and better resistance to high salinity than HPAM.
Nowadays, there is a wide range of available co-polymers and ter-polymers tolerant to high salinity, divalent ions and temperature for different applications (as shown on figure 1) (Vermolen, 2011). These copolymers would be suitable to prepare injection slugs using produced water with high salinity; this option has a great potential for field applications with favourable economic consequences in saving fresh water and protecting environment.

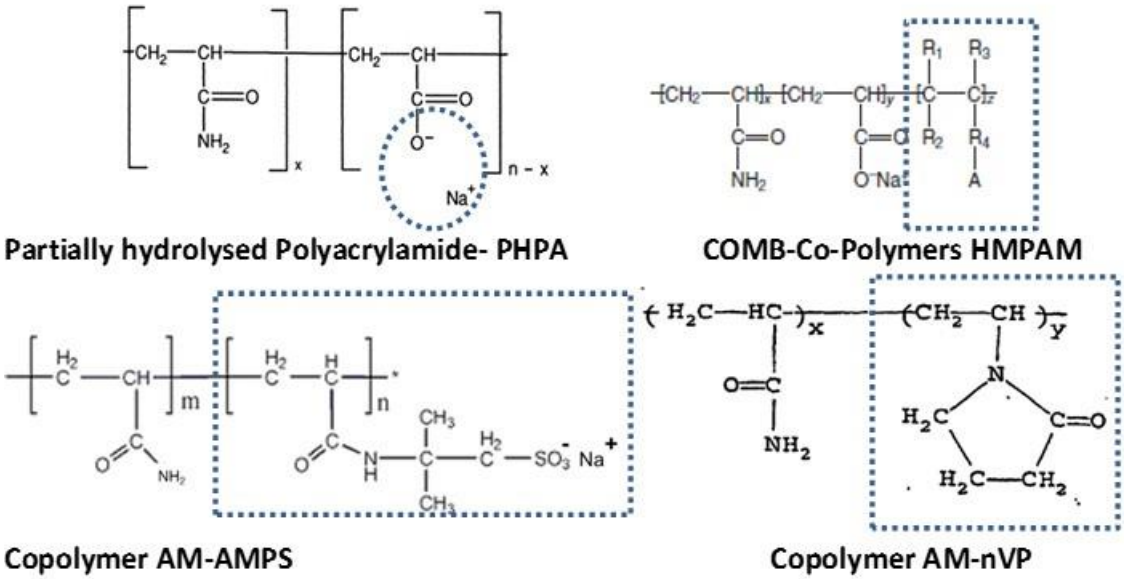

Figure 1 *Chemical structure of polymers and co-polymers acrylamide tested.*

Methods of polymer screening for polymer flooding has been object of many studies as the behaviour of the associated polymer solutions is affected by different parameters; some of them are presented on figure 2. Reservoir properties, composition of formation fluids, temperature, flow conditions and polymer structure will affect the effectiveness of polymer flooding. Therefore, all those variables need to be previously evaluated in the laboratory to find the optimal polymer for a particular application, and also well represented by mathematical correlations in reservoir simulation. While the main mechanism reported for increasing viscosity solutions of PHPA is by charge repulsion and molecular elongation of the polymer, both repulsion and intermolecular association above a critical concentration for HMPAM has been reported by Taylor et al (1995) as referred by Levitt (2008).

As the properties of polymeric solutions are strongly linked to ionic interactions, variables such as the distribution of ionic charge along the polymer, the length of the hydrophobic monomers, the molecular weight of the polymer and polymer concentration are affected by the ionic composition and salinity of both the formation brine in the porous media and water used for injection. The object of this research was to study the effect of flow behaviour of HPAM (hydrolysed poly-acrylamide) of different molecular weight (MW) and special co-polymers as chemical flooding of sandstones core rocks under high salinity conditions, and under harsh conditions of brine composition existing in the North Sea.

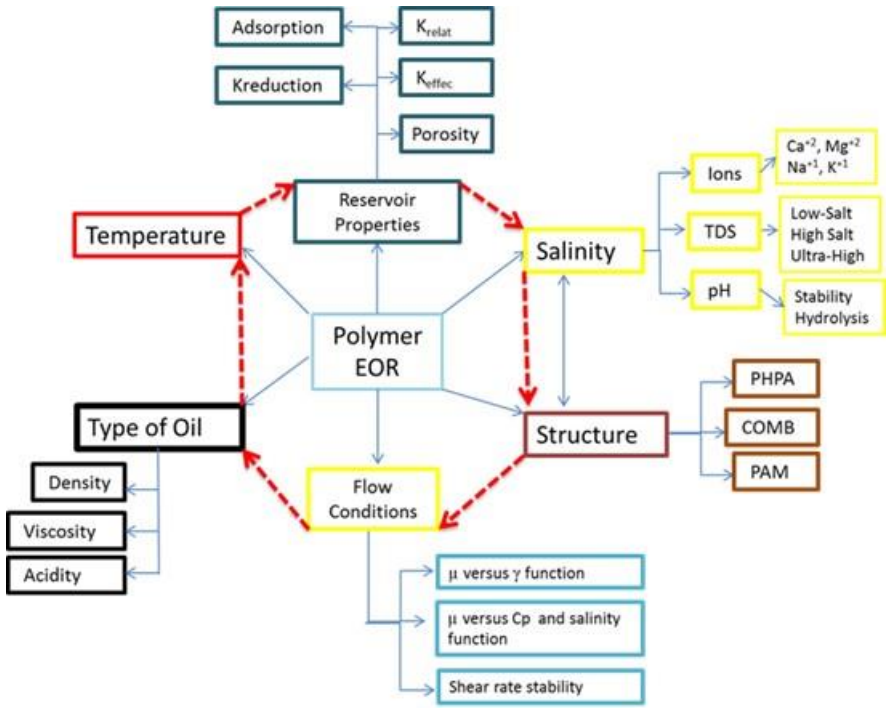

Figure 2 *Variables for screening Polymers for EOR applications.*

Theory

Screening of Polymers for EOR applications

There are several physical and chemical interactions involved in the Polymer flooding process, as polymer solutions will be in contact with existing conditions in the porous media; the fluid will be deformed by the permeability and pore network of the reservoir. The success of a particular application depends on the appropriate selection of the polymer solution to be injected considering reservoir properties and location conditions (Melo et al, 2008).
The more important properties for a polymer to be evaluated before injecting into the reservoir are: viscosity, salinity and calcium tolerance, mechanical and thermal stability, injectivity, and transport conditions (Levit, 2009). Wang and Dong (2009) studied the effect of effective viscosity of polymer on oil recovery for different oil viscosity and found a minimum and maximum value of effective viscosity of polymer required for any crude oil viscosity at constant permeability. Higher polymer concentration was required for higher viscosity but there was an optimal concentration for each case, polymer solutions were tested at fixed shear rate. After the optimal polymer concentration, other interactions seem to prevent higher polymer concentration to increase oil recovery.
The increase viscosity of aqueous solution of polymers PHPA has been explained as an extension of the polymer by repulsion of negatively charges due to carboxylic groups distributed along the polymer chain which is related with the grade of hydrolysis and also by the size of the molecule or molecular weight, this charge repulsion is shielded by the presence of ions on the solution with the consequent viscosity reduction. Divalent ions have a major effect than monovalent ions. For PHPA, the higher the grade of hydrolysis the stronger the shielding effect on viscosity is for high salinity conditions. A study by Peng and Wu as cited by Weber et al (2011) investigated the formation of self-complex HPAM on the presence of $Ca^{2+,}$ depend on the concentration of Ca^{2+} and the anionic grade of HPAM. They reported different interaction as a result of salinity, intra-chain, interchange or formation of complex of polymer with Ca^{2+}.

Physical chemical interactions are more complex for co-polymers and ter-polymers as they have two type of charge one from the carboxylic group and other functional groups existing in the monomer which can polarize the molecule and also form complex with divalent ions, the resultant viscosity can be different according with the interaction and resultant hydrodynamic molecular ratio.
For hydrophobic modified polymers type comb HMPAM, hydrophobic and hydrophilic groups are introduced in the co-monomer to increase the rigidness of the molecule and create stereo and electric repulsion between hydrophilic and lipophilic and, also between hydrophilic and carboxylic groups. These electric and steric interactions increase the hydrodynamic radio of the molecule and therefore the viscosity (Beijing Hengju, no-date; Sheng, 2011). HMPAM polymer molecules form a series of entangled temporary network where both tangles and hydrophobic interactions are present in polymeric solutions (Weber et al, 2011) with consequences on rheological behaviour. As a result of these different interactions, the flow behaviour under high salinity conditions and shear rate needs to be rigorously evaluated before any particular application. Adjust variables and mathematical correlations required to simulate polymer flooding EOR.

Mathematical correlations for Polymer Flooding

In order to simulate the flow behaviour of polymer flooding into the reservoir some mathematics models have been developed to represent the dependence of viscosity with polymer concentration, salinity, shear rate, and reservoir permeability (Sheng,2011). UTCHEM is a model that allows simulating 3 dimensions, multicomponent, multiphase, compositional model of chemical flooding EOR (UTCHEM, 2009).
For the dependence of viscosity with polymer concentration and salinity UTCHEM uses Flory-Huggins (Sheng, 2011; UTCHEM, 2009) equation which can be represented by equation 3, this equation allows the estimation of polymer viscosity.

$$\mu_p^0 = \mu_w\left(1+\left(A_{p1}C_p + A_{p2}C_p^2 + A_{p3}C_p^3\right)C_{sep}^{S_p}\right) \quad (3)$$

Where the factor C_{Sep}^{Sp}represents the dependence with salinity and hardness (divalent ions), Sp can be estimated by the slope of the log-log plot of $\frac{\mu_p^0-\mu_w}{\mu_w}$ versus Csep and, βp is a parameter to adjust the correlation.
A_{P1}, A_{P2}, A_{P3} are constants obtained through matching with experimental data,
μw is the brine viscosity, Pa·s
Cp is the polymer concentration in brine, kg/m^3
μp_0 – zero shear viscosity, Pa·s
Csep is the effective salinity for polymer in Eq/m^{3}and can be calculated by using equation 4;

$$C_{sep} = \frac{C_{51}+(\beta_p-1)C_{61}}{C_{11}} \quad (4)$$

C_{11} - water concentration in the aqueous phase, fraction
C_{61} – divalent concentration in the aqueous phase, Eq/m^3
C_{51} – anion concentration in the aqueous phase, Eq/m^3

The dependence of polymer viscosity on shear rate will be modelled by using Meter's correlation (Meter and Bird, 1964) as cited by Sheng (2011) and can be represented by equation 5.

$$\mu_p = \mu_w + \frac{\mu_p^0 - \mu_w}{1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_{1/2}}\right)^{(p\alpha - 1)}} \quad (5)$$

Where
μw – brine viscosity, Pa·s
γ – shear rate, s^{-1}
$\gamma_{1/2}$ - shear rate at which viscosity is the average of μw and μp0, s^{-1}
μp_0 – zero shear viscosity, Pa·s
Pα - empirical parameter obtained by matching laboratory data
μ_p – apparent polymer viscosity, Pa·s

Experimental Methods

Materials

In order to complete the study, a series of experiment were completed in the laboratory for each polymer following the variables for screening polymers, materials and methods are shown on figure 3. A sandstone reservoir represented by core samples of Bernheimer with the properties detailed on table 1 was selected for this study.

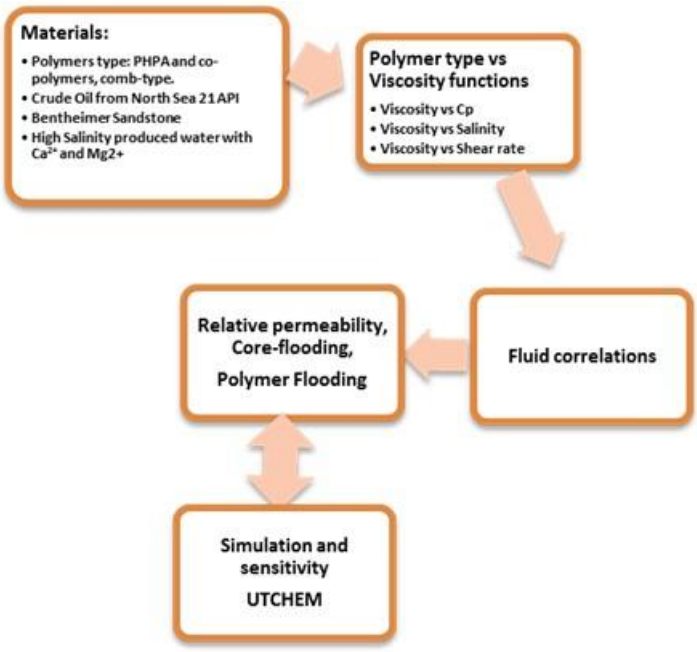

Figure 3 *Schematic representation of materials and methods.*

Synthetic brine was prepared considering a published composition of high salinity produced water from Gryphon field located in the North Sea, details of composition are shown on table 2.

Table 1 *Crude oil and Bentheimer characteristics.*

Rock type	Berntheimer Sandstone
Permeability	570 mD
Porosity	0.178 frac
Crude Oil Type	Acidic Heavy Oil
API	21
Viscosity (Dead oil) (25 C)	370 mPa

Table 2 *Synthetic brine composition from North Sea Reservoir Produced water (Mansel et al, 1994).*

Ion	Total mass of ions in brine (mg/L)	Equivalent concentration mEq/mL
Na^+	22330	0.97087
K^+	299	0.007667
Ca^{2+}	1860	0.093
Mg^{2+}	975	0.08125
Cl^-	40830	1.150141
TDS	62,264	

A series of polymers PHPA of different molecular weight and the same hydrolysis grade (anionic grade) were evaluated and compared with polymers AM-AMPS, AM-nVP and Comb-Co-Polymers, details of polymers are shown on table 3.

Table 3 *Characteristics of Polymers evaluated.*

Polymer type	Molecular weight	Composition	Active fraction of polymer, %
PHPA -6	High	25 - 30 % anionic	90
PHPA-5	Medium High	25 - 30 % anionic	90.9
PHPA-4	Medium	25 - 30 % anionic	89.9
PHPA-3	Low	25 - 30 % anionic	91.2
AM-AMPS	Low	25 - 30 % anionic	90.3
AM-n-VP	High	25 - 30 % anionic	89.9
HMPAM-1	Medium High	25 - 30 % anionic	88.0
HMPAM-2	Low	25 - 30 % anionic	88.0
HMPAM-3	High	25 - 30 % anionic	88.0
HMPAM-4	Ultra-High	25 - 30 % anionic	88.0

Measurement of viscosity functions for different type of polymers

To evaluate the effect of the type of polymer on salinity, hardness and shear rate resistance, Polymer solutions were prepared according with recommended procedures of mixing established by the manufacturer. Each type of polymer was dissolved in distilled water and in synthetic brine to obtain a concentration of 5000 ppm. The general procedure to prepare a 5000 ppm polymer solutions was to weight (1 / (1000*X)) kg of polymer powder was mixed with ((200 -1 / X) / 1000) kg of brine, where X represents the active fraction of polymer (frac). Then these initial solutions were used for preparation of the wide variety of solutions with different polymer concentration and salinity (by

additional mixing with distilled water and brine). Polymer solutions were prepared using a RPM controlled mixer sprinkling the polymer at 700 rpm in order to create strong vortex and for better dissolution of polymer powder. Polymers were added very slowly in order to prevent aggregation of hydrated particles. After all powder mixed, were left for 2 hours for thorough mixing at 200 rpm.

To investigate the effect of polymer concentration on the rheological behaviour of polymeric solutions each type of initial polymer solutions (5000 ppm of polymer in brine) were diluted by brine to concentrations to 100, 500, 1000, 2000, 3000 and 4000 ppm of polymer in brine. Likewise, the effect of different salinities on rheology of polymer solutions was investigated. For these purposes, each 5000 ppm polymer solution in brine (100% salinity) was mixed with 5000 ppm polymer solution in distilled water (0% salinity) to obtain solutions with effective different salinities of $2.75 \cdot 10^{-3}$, $2.2 \cdot 10^{-3}$, $1.65 \cdot 10^{-3}$, $1.1 \cdot 10^{-3}$ and $0.55 \cdot 10^{-3}$ eq/m^3 by keeping polymer concentration constant.
Viscosity test were performed by using a Bohlin Gemini rotational rheometer with cone and plate type measuring unit. Lower plate of 6·10-2 m fixed plate with thermal regulation and upper cone of $4 \cdot 10^{-2}$ m rotating cone with 4° angle. Three types of viscosity tests were carried out: creep test, oscillation test and viscometry test.

Relative Permeability, core –flooding, Polymer flooding:

An unsteady state water flood experiment was used to determine the two-phase relative permeability as well as oil recovery. In order to model two phase relative permeabilities, Corey type curves were used to adjust relative permeability curves, (Brooks and Corey, 1966) as cited by Tarek (2001). The schematic core flood procedure is presented in Figure 4. Relative permeability curves were adjusted by fixing experimental results.

$$k_{rw} = k_{rw}^{o}\left(\frac{S_w - S_{iw}}{1 - S_{iw} - S_{or}}\right)^{n_w} \qquad k_{ro} = k_{ro}^{o}\left(1 - \frac{S_w - S_{iw}}{1 - S_{iw} - S_{or}}\right)^{n_o} \tag{6}$$

S_w - saturation of water, fraction
S_{iw} - residual saturation of water, fraction
k_{rw}^{o} – relative permeability endpoint of water, fraction
k_{ro}^{o} – relative permeability endpoint of oil, fraction
S_{or} - residual saturation for oil, fraction
k_{rw} - relative permeability of water, fraction
k_{ro} - relative permeability of oil, fraction
n_0 - curvature of the relative permeability curve for oil, dimensionless
n_w - curvature of the relative permeability curve for water, dimensionless

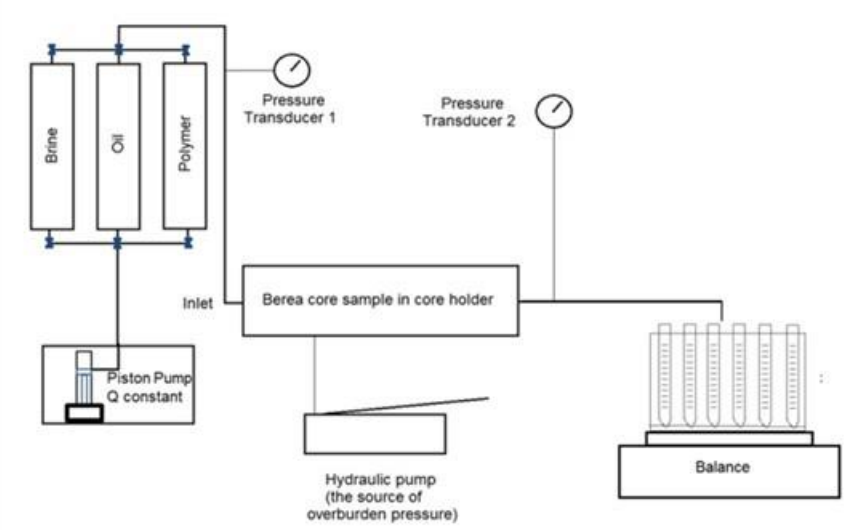

Figure 4 *Diagram of Core flooding Equipment*

Results and discussion

Imbibition and drainage experiment were matched using a combination of software SENDRA for a 1D model to get a first approach of the relative permeability curve using Corey mathematical correlation (equation 6) and with a 2D model using UTCHEM. Figure 6 represents the relative permeability curve obtained for imbibition. Corey parameters are represented on equation 7.

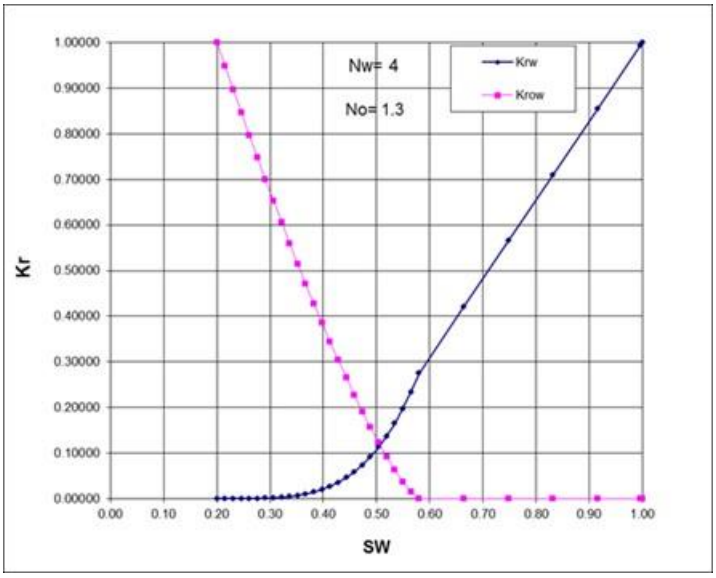

Figure 5 *Relative Permeability.*

$$K_{rw} = K_{rw}^{0}\left(\frac{S_w - 0.2}{1 - 0.2 - S_{or}}\right)^{4} \qquad K_{ro} = K_{ro}^{0}\left(\frac{S_w - 0.2}{1 - 0.2 - S_{or}}\right)^{1.3} \tag{7}$$

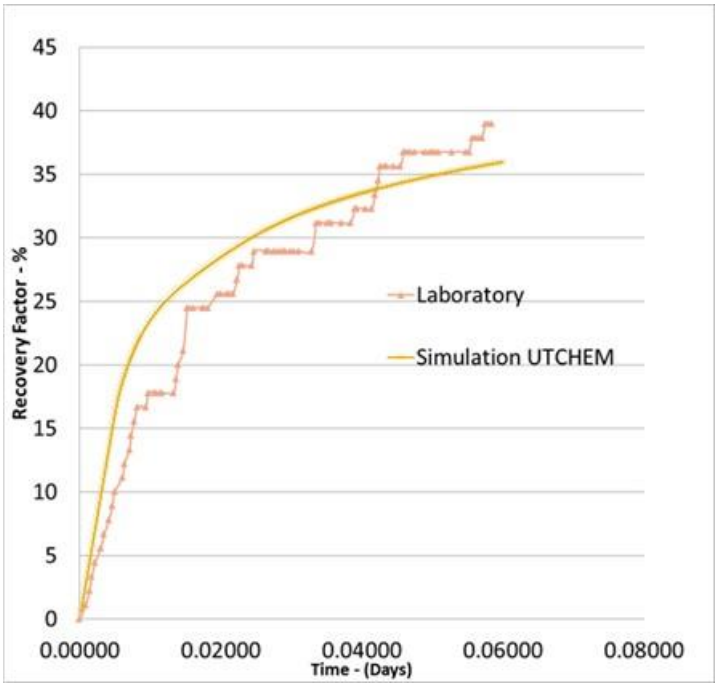

Figure 6 *History match of core water-flooding with UTCHEM*

A 2D model (x:1, y:20, z:5) for the core flooding was created using UTCHEM and results from history match of water-flooding are presented on figure 7, the simulation slightly overestimated the cumulated oil at the beginning and underestimated at the end, results are reasonable within a good range it may be due to flow rate fluctuations on experimental results. 3 dimensional results from UTCHEM were processed using Kraken 2.4 software from ESSS (www.esss.com.br) and a visual of final oil saturation after water-flooding is presented on figure 8. Oil saturation are lower at the bottom despite of the fluid is injected at the centre of the core, it is an indication of a slightly gravity effect between oil and water affecting the process.

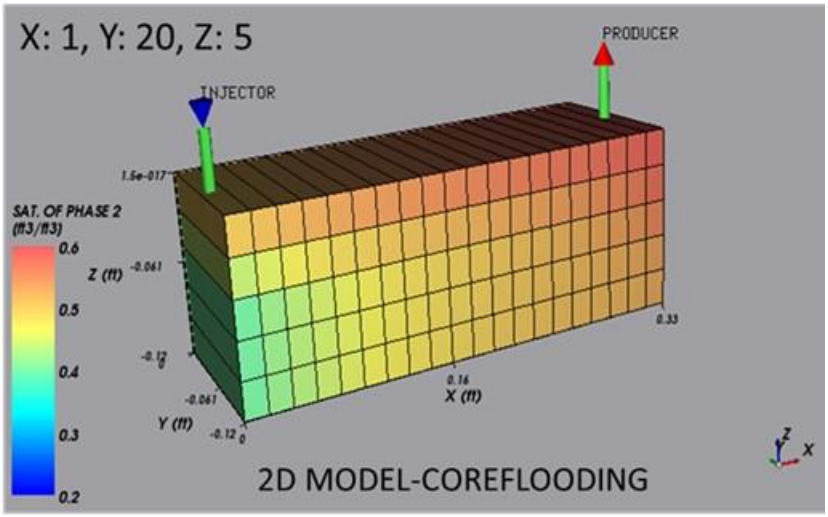

Figure 7 *2D model of Oil saturation profile after water-flooding.*

Fluid Properties and flow correlations for UTCHEM

The effect of polymer concentration on viscosity for the polymers is presented on graphs 9 to 11, as it was expected, viscosity of polymer increases with polymer concentration at high salinity, higher viscosity are obtained for HMPAM polymers. The higher the polymer concentration is, the bigger the differences in viscosity for the different polymers are. There is a minimal polymer concentration

required to get higher viscosities effect by molecular weight. It is 0.1% for PHPA and co-polymers AM-AMP and AM-n-VP and not minimal for HMPAM. PHPA polymer molecules tend to contract under salinity conditions by shielding of ionic charges along the molecule by cationic ions on the solution, this effect is minimized on HMPAM because the hydrophilic and hydrophobic groups minimize the shielding effect and also decrease the flexibility of the molecule by both steric and ionic forces.

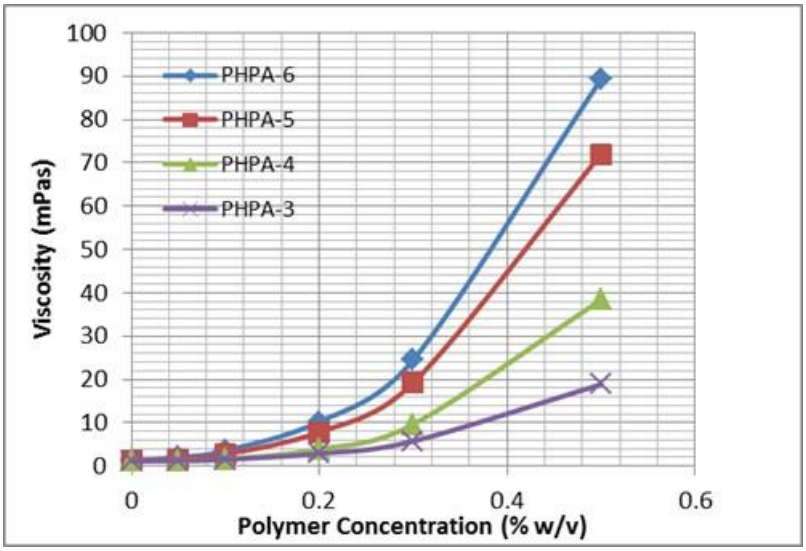

Figure 8 *Viscosity vs Polymer Concentration for PHPA polymers on Hard Brine.*

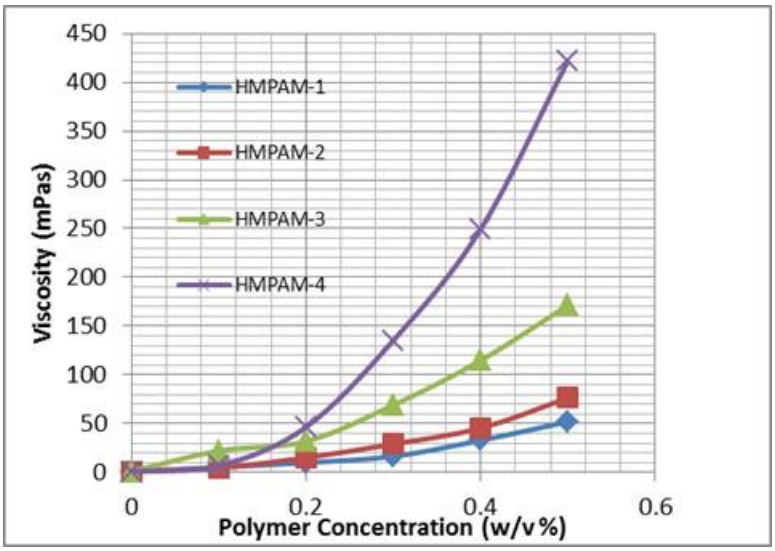

Figure 9 *Viscosity vs Polymer Concentration for HMPA polymers and Co-Polymers on Hard Brine.*

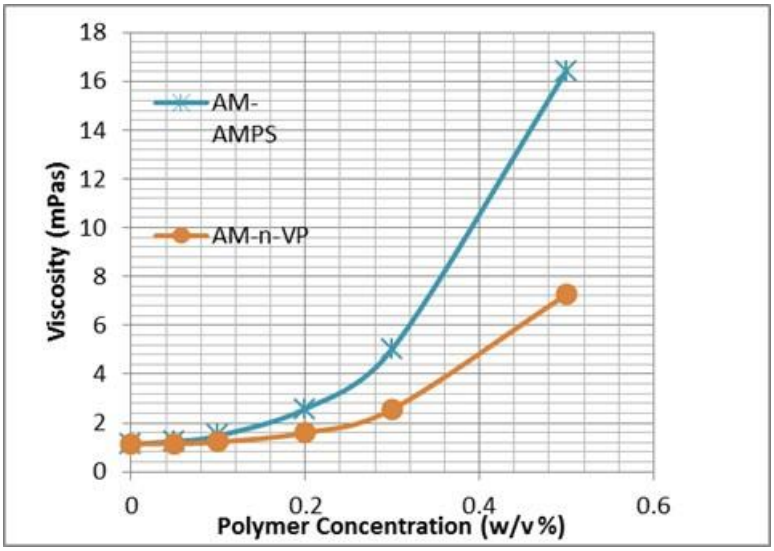

Figure 10 *Viscosity vs Polymer Concentration for Co-Polymers on Hard Brine.*

The viscosity of polymer AM-AMPS and AM-nVP is lower than the rest of polymers and, despite the AM-nVP polymer having higher molecular weight than AM-AMPS, the MW is not reflected on their viscosity behaviour. Vermolen et al (2011) reported intramolecular or intermolecular interactions for co-polymers depend on salinity and formation of complex with divalent ions. The inflection point for increasing viscosity is 0.1% for AM-AMPS polymer and 0.2% for AM-n-VP polymer. Therefore, less concentration of AM_AMPS is required to increase concentration. The effect of salinity on the viscosity of polymers PHPA, co-polymers PAM and hydrophobic modified polymers HMPAM, is presented on figure 12 and 13, viscosity values drop with the increase of salinity for all polymers, apparent viscosity values for HMPAM are more than 30% higher than the rest of the polymers for the range of salinity evaluated, as reported by the manufacturer (www.hengju.com). Co- polymer AM-n-VP keep almost constant viscosity for the range of salinity, the same behaviour was observed by the co-polymer AM-AMPS between 3.5 to 4.8 % salinity. The effect of molecular weight on the viscosity of PHPA is minimal compare with the effect of salinity at high salinity >3.5 %. The behaviour of HMPAM is more complex with the increase of salinity, there is a high decrease on viscosity until about 4% salinity after that the polymers tend to stabilize around a constant value of viscosity for HMPAM-1 and HMPAM-2 (Medium and Low MW) and for HMPAM-3 and HMPAM-4.

Experimental results of viscosity versus polymer concentration, salinity and shear rate for the different polymers were adjusted using Flory-Huggins correlation, defined on equation 3. Results for the polymers are presented on tables 4 and 5.

$$\frac{\mu_p^0 - \mu_w}{\mu_w}$$

Sp parameter obtained by the slope of vs Csep, reflect the effect of salinity on apparent viscosity, all the values are negative indicating a decrease on viscosity by the salinity effect, and absolute values are higher for HMPAM which reflect a major effect of salinity on viscosity. Absolute values of Sp increase with MW for PHAP and co-polymers and decrease with MW for HMPAM. Apparent viscosity of HMPAM is more than 3 times higher than the viscosity of PHPA at high salinity.

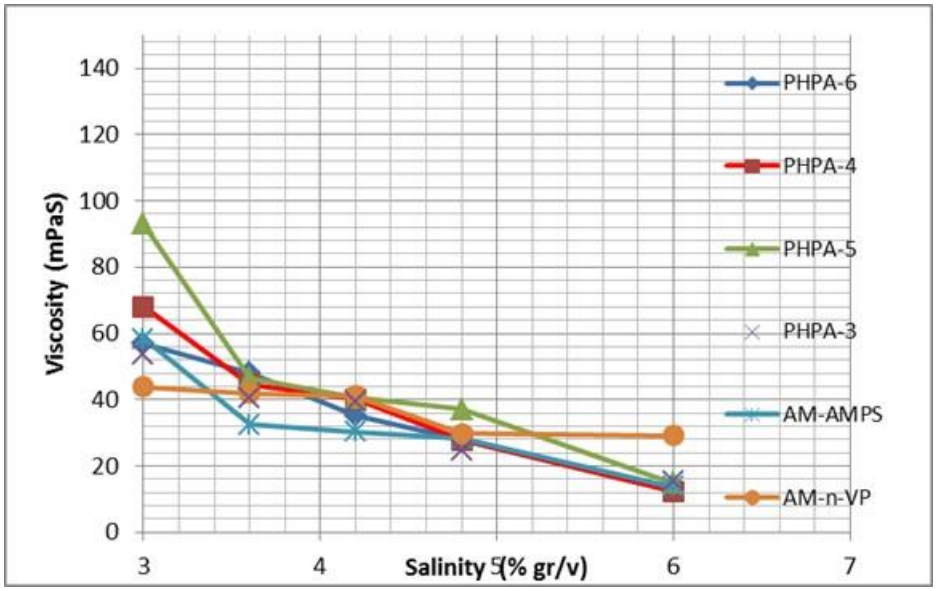

Figure 11 *Viscosity vs Salinity for PHPA polymers and Co-Polymers.*

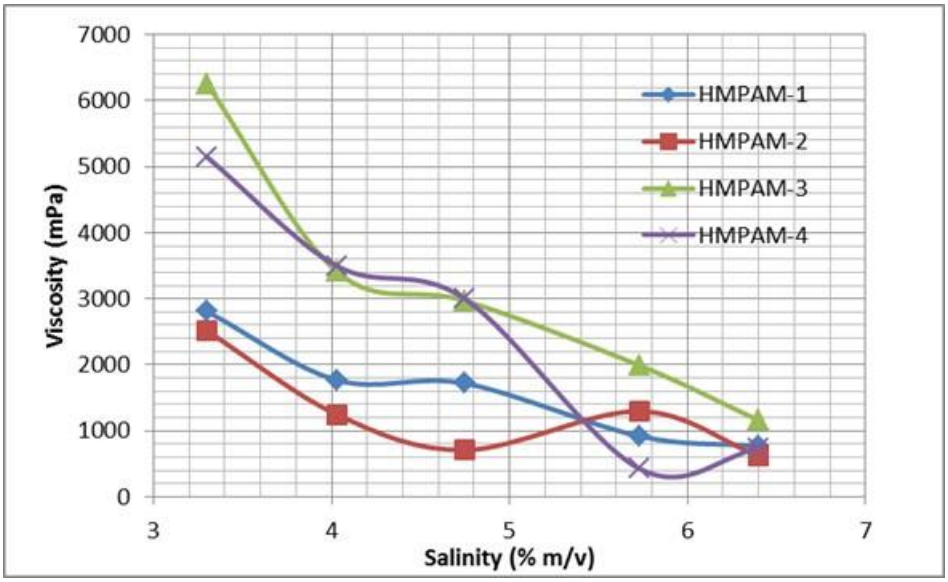

Figure 12 *Viscosity vs Salinity for HMPAM polymers.*

Experimental results of viscosity versus shear rate for the different polymers were adjusted using Meter's correlations (Meter and Bird, 1964) defined on 5 and matching parameters are presented on tables 6 and 7. Results from model were also included as points on graphs presented on figures 14 and 15.PHPA polymers and PAM co-polymers have similar behaviour, Newtonian at lower shear rate (< 10 s-1) and non- Newtonian shear thinning behaviour at shear rate higher than 10 s-1 as is shown on figure 14, similar behaviour has been found for polymer PHPA on saline solutions (Levitt, 2009; Sheng, 2011). HMPAM polymers have mainly non- Newtonian shear thinning behaviour on the evaluated range of shear rates (0.1-100 s-1) . Typical shear rates expected in a reservoir are on the range of 1-10 Sec-1 depend on permeability, porosity and flow rate. Viscosity of the solution is more affected by shear rate for HMPAM polymers than for PHPA and co-polymers.

Adjusted Meter's Pα shown on tables 6 for polymers PHPA are similar and slightly increase with the MW of the polymer, while for HMPAM values are lower for higher MW polymers (HMPAM-3 and HMPAM-4). Values of $\gamma_{1/2}$ for PHPA and co-polymers are higher than for HMPAM polymers which

are related with the range of Newtonian behaviour. HMPAM are mainly no-Newtonian and is revealed by their low $\gamma_{1/2}$ values. The higher is the value $\gamma_{1/2}$, the smaller is the effect of shear rate on viscosity for the polymers. For PHPA the higher the molecular weight, the shorter the range of Newtonian behavior and $\gamma_{1/2}$ values are. For HMPAM an opposite behavior is found, the higher the MW is the higher $\gamma_{1/2}$ values are. Co-polymers AM-AMPS and AM-nVP have similar Newtonian and no-Newtonian behavior with higher apparent viscosities for AM-AMPS polymer.

Table 4 *Parameters of PHPA polymers for Flory-Huggins correlation.*

	PHPA-6	PHPA-5	PHPA-4	PHPA-3
A_{p1}	3	0	11	2
A_{p2}	350	435	143	124
A_{p3}	1200	545	1000	654
$C_{sep}(eq/m^3)$	3.06	3.07	2.7458	2.7458
S_p	-0.49	-0.47	-0.43	-0.35
μ_w(Pas)	1.14	1.14	1.14	1.14

Table 5 *Parameters of HMPAM polymers for Flory-Huggins correlation.*

	HMPAM-1	HMPAM-2	HMPAM-3	HMPAM-4	AM-n-VP	AM-AMPS
A_{p1}	50	180	600	70	4	17
A_{p2}	45	1000	900	1080	22	14
A_{p3}	500	1000	2200	2800	232	147
$C_{sep}(eq/m^3)$	2.978	1.889	2.875	1.779	2.72	2.37
S_p	-1.256	-3.118	-1.633	-1.018	-0.31	-0.24
μ_w(Pas)	1.97	1.14	1.17	1.17	1.14	1.14

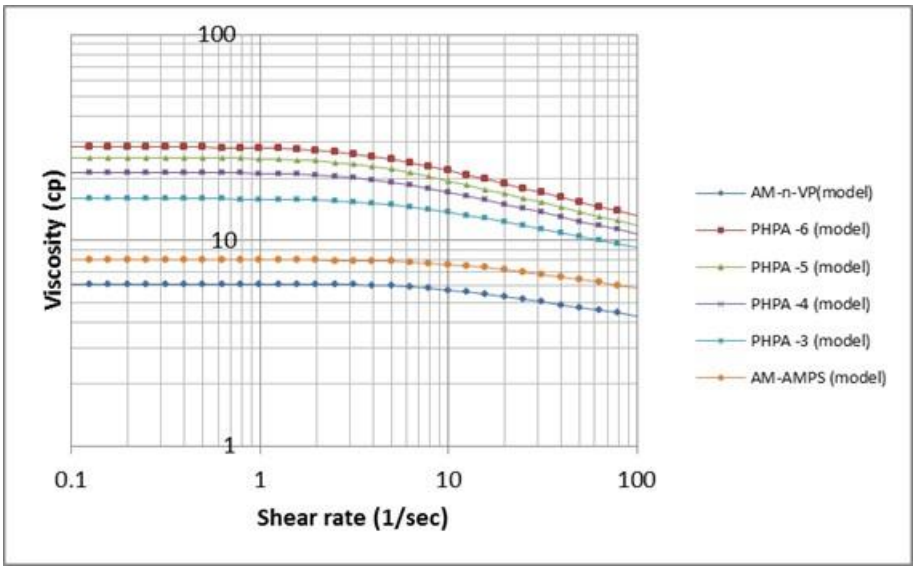

Figure 13 *PHPA and Co-Polymers Viscosity vs Shear rate (Meter's Model Fitting).*

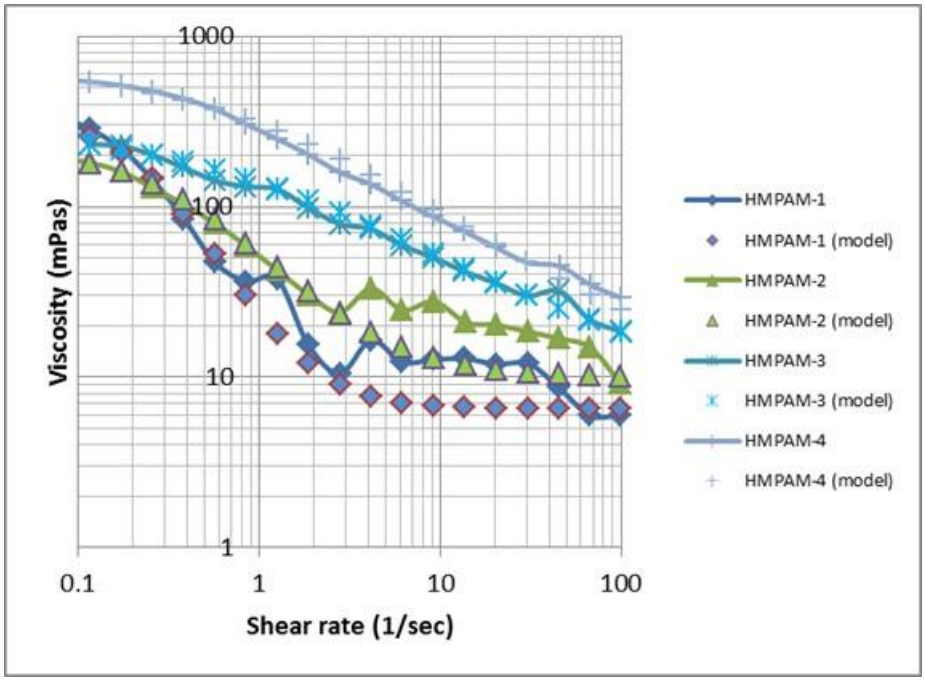

Figure 14 *HMPAM Viscosity vs Shear rate (Meter's Model Fitting).*

Table 6 *Parameters for PHPA polymers in hard brine for Meter's correlation.*

	PHPA-6	PHPA-5	PHPA-4	PHPA-3
μo, mPa.s	28.41	25.16	21.31	15.92
μ∞, mPa.s	1.14	1.14	1.14	1.14
Pα	1.72	1.72	1.69	1.68
$\gamma_{½}$ (1/sec)	58.76	58.76	68	90

Table 7 *Parameters for HMPAM polymers in hard brine for Meter's correlation.*

	AM-AMPS	AM-n-VP	HMPAM-1	HMPAM-2	HMPAM-3	HMPAM-4
μo, mPa.s	8.02	6.16	335.6	218	293	659
μ∞, mPa.s	1.14	1.14	6.5	10	1.14	2.5
Pα	1.9	1.95	2.9	2.3	1.59	1.74
$\gamma_{½}$ (1/sec)	180	140	0.22	0.36	0.75	0.88

Simulation results:

Results from fluid properties and core-flooding were used to model and history match of water-flooding and polymer flooding and the matched for HMPAM-3 is shown on figure 16, there is a reasonable agreement with experimental data and simulation, except that for laboratory results the limit of residual oil saturation is slightly overcome, what may imply some modification of capillary

forces in addition to viscosity. HMPAM contain hydrophilic and hydrophobic groups along the PAM chain which may modify interfacial tension between oil and water.

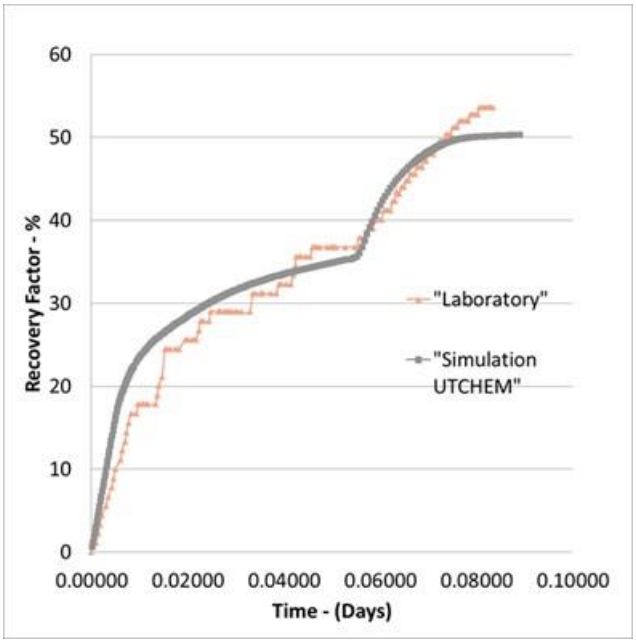

Figure 15 *History matching of water-flooding and polymer flooding for HMPAM-3 with UTCHEM.*

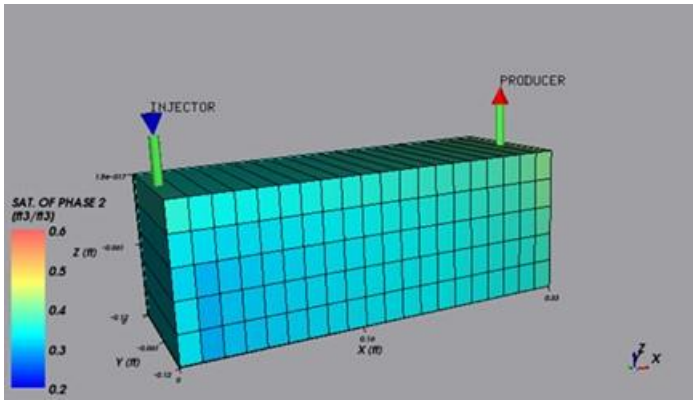

Figure 16 *2D model of Oil saturation profile after polymer-flooding.*

Simulation results for oil saturation after polymer flooding for HMPAM-3 is presented on figure 17, there is an excellent sweeping efficiency and oil overall recovery result for this polymer. Cumulated oil as a result of a sensitivity analysis with all the evaluated polymers are presented on figures 18 and 19. For PHPA polymers the higher the MW the higher the oil recovery was, except for PHPA-3 which has higher oil recovery than polymer PHPA-4. For HMPAM polymers only HMPAM-3 and HMPAM-4 improved oil recovery with similar results despite them have different MW.

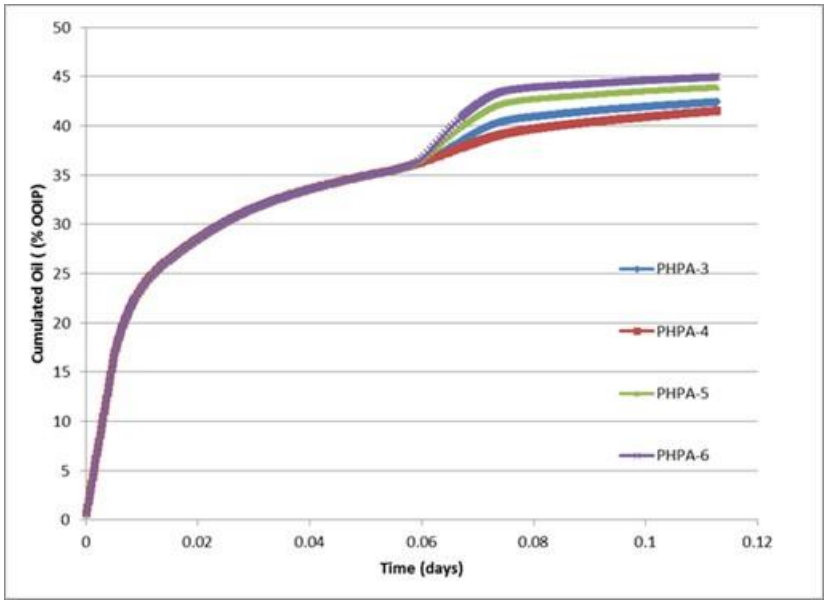

Figure 17: Sensitivity analysis of water-flooding for PHPA polymers

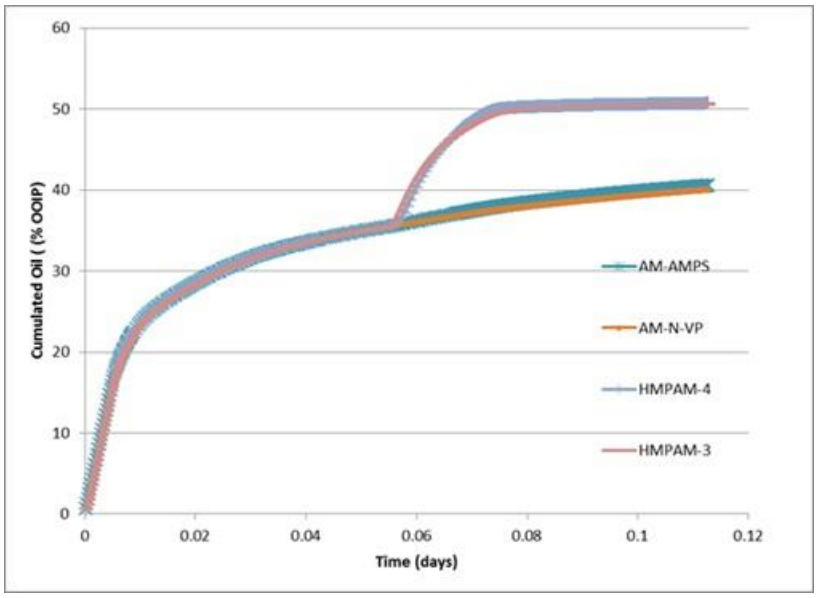

Figure 18 *Sensitivity analysis of water-flooding for co-polymers.*

Simulation results for oil saturation of all cases are presented on figure 20. Despite HMPAM-3 and HMPAM-4 have almost similar results for cumulated oil on the graph displayed on figure 18, they showed differences on final oil saturation after polymer flooding, thus HMPAM-3 polymers had better sweeping efficiency than HMPAM-4 polymer despite their MW and viscosity values, this result support findings of Wang and Dong (2009) related with an optimal viscosity for oil recovery. Despite of PHPA have more than three times lower viscosity than HMPAM, and lower viscosity than the crude oil (300 mPa) is effective on increasing oil recovery on high salinity conditions. It seems Newtonian behaviour allows them to push the oil compared with shear thinning behaviour of HMPAM. HMPAM-1 and HMPAM-2 Polymers (Low and Medium

molecular weight) did not increase oil recovery, at higher concentration of 0.5% was required to get results.

Conclusions

• Core flooding experiments were matched with 1D simulations to study two phase flow in the porous media and adjust relative permeability.
• Flow correlations for the polymers were evaluated and mathematical correlations were fitted for simulation.
• While polymers PHPA and co-polymers showed Newtonian behaviour at low shear rates and non-Newtonian at high shear rates, HMPAM polymers have shear thinning behaviour.
• Newtonian behaviour on PHPA-3 is seems to support its higher recovery factor comparing with PHPA-6 (higher MW)
• Viscosity of HMPAM is more sensible to polymer concentration showing higher viscosities than PHPA polymers.
• Though polymers with high MW are more effective increasing polymer viscosity, ionic interactions play an important role at high salinity, viscosity needs to be evaluated.
• Co-polymer AM-AMPS is less sensible to salinity but requires higher concentrations.

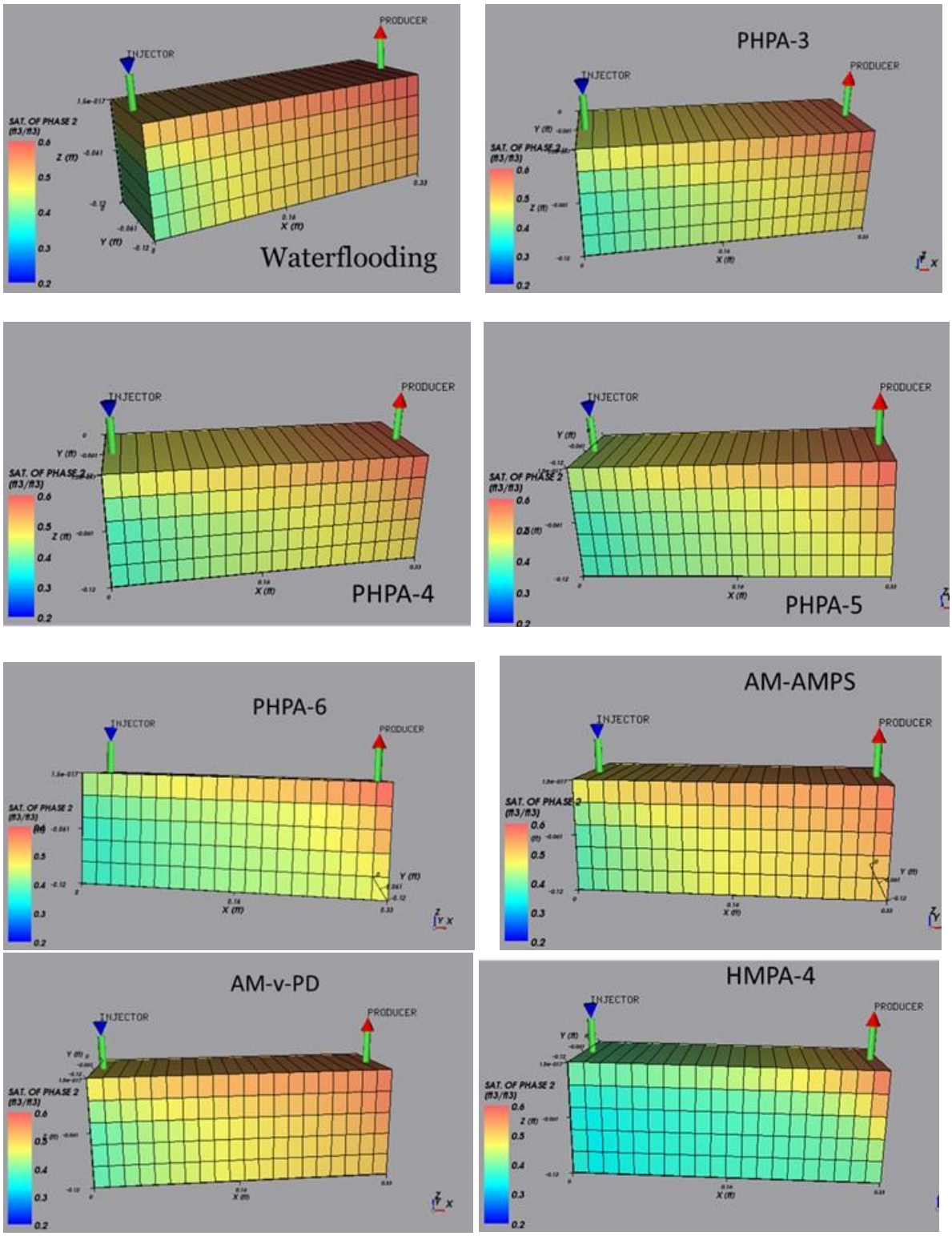

Figure 19 *2D model of Oil saturation profile after polymer-flooding for evaluated polymers.*

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